

Activation of Small Molecules by Cluster Complexes

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Abstract—The results of theoretical and experimental investigations on activation of small molecules on their coordination to cluster complexes of heavy transition metals with weak- and strong-field ligands are presented. Homogeneous catalytic redox reactions of the CO, N₂, H₂O molecules and the N₃[−] molecular anion in the presence of cluster complexes of low-valent molybdenum and rhenium are studied. The reaction mechanism is established. Three modifications of the homogeneous cluster catalysis of redox reactions of small molecules are described.

INTRODUCTION

The subject of the article is a phenomenon intriguing by its simplicity, elegance, and purposefulness and very interesting practically in terms of organization of technological processes and cognizing vital functions. The case in point is activation of small molecules on their coordination to cluster complexes (M_nL_m) of heavy transition (4d, 5d) metals with strong- and weak-field ligands. Small molecules are implied as molecules and molecular ions consisting of two, three, or four atoms each containing small number of electrons, such as CO, N₂, H₂O, HCN, O₂, CO₂, C₂H₂, CN[−], or N₃[−].

Activation, as decrease in the total energy of bonds of a molecule on its coordination to a certain center, is a consequence of electronic rearrangement of the molecule. Orbital interactions between a molecule and a coordinating center generally involve frontier, i.e. highest occupied and lowest unoccupied, molecular orbitals (HOMO and LUMO). These interactions are electron-donor and electron-acceptor in their nature. Coordination-induced electronic effects reflect electron charge transfer from the molecule to the coordinating center and back, depending on characteristics of interacting orbitals. The following statement is evident: decrease in the total bond energy of a molecule and, therefore, activation of the molecule by its coordination to a coordinating center strengthens, as the electron population of occupied bonding MOs decreases in the course of electron charge transfer from these MOs to orbitals of the coordinating center and population of vacant (in an isolated molecule) antibonding MOs in the course of electron charge transfer to these MOs from orbitals of the coordinating center. These, opposite-“in-direction,” electron

transfers mutually facilitate each other (synergistic effect) and, above all, restrict or even prevent development of unrealistically high electrostatic charges on atoms composing interacting molecular systems, in full agreement with the known Pauling electroneutrality principle.

ELECTRONIC ACTIVATION EFFECTS. THEORETICAL MODEL

A theoretical model was developed [1, 2] to describe the electronic rearrangement of small molecules on their coordination to transition metal atoms M. A parameter measuring the activating action in this model is the electron density redistribution on the donor–acceptor interactions K–S accompanying coordination of a small molecule S to a coordinating and, simultaneously, activating center K.

First of all, it was established what properties (electron-donor or electron acceptor) of center K and molecule S should be preferred for effective activation of the molecule. Phenomenological concepts are rather trivial. If there are low-lying vacant antibonding π^* MOs in the electronic structure of molecule S, the activation is based on the π -acceptor ability of S and π -donor ability of K ($K-\pi\bar{e}\rightarrow S$), i.e. the destabilization of S is mostly contributed by vacant antibonding π^* MOs of the latter. If, however, S lacks such π^* MOs and its highest occupied bonding orbitals are σ MOs, the activation is based on the σ -donor ability of S and σ -acceptor ability of K ($K\leftarrow\sigma\bar{e}-S$), i.e. the destabilization of S is mostly contributed by its occupied bonding σ MOs. However, abundant evidence is available showing that even if there are no energetically suitable vacant π^* MOs in the electronic structure of S and vacant σ^* MOs have high energies (typically higher than the vacuum level), the molecule is

activated by accepting electrons on its vacant antibonding σ^* MOs from the coordinating donor center ($K-\sigma\bar{e}\rightarrow S$).

To resolve this alternative, the mechanism of bond activation in diatomic molecules XY by transition metal atoms M considered, in terms of the simple MO LCAO theory in the frontier orbital approximation. The valent electronic structure of XY is described by a bonding and an antibonding MOs of σ and/or π type:

$$\varphi = [2(1 + S)]^{-1/2}(\chi_1 + \chi_2), \quad \varphi^* = [2(1 - S)]^{-1/2}(\chi_1 - \chi_2)$$

with relative energies

$$\varepsilon(\varphi) = \alpha + \Delta \text{ and } \varepsilon^*(\varphi^*) = \alpha - \Delta^*,$$

where $\Delta = (\beta - \alpha S)/(1 + S)$ and $\Delta^* = (\beta - \alpha S)/(1 - S)$; α , β , and S are the Coulomb, resonance, and overlap integrals, respectively; and χ_1 and χ_2 are the valent orbitals of atoms X and Y.

The molecular orbitals φ and φ^* are unsymmetrically split with respect to the energy α of the corresponding atomic orbitals χ_1 and χ_2 ; ε^* is heightened stronger than ε lowered; indeed, $\Delta^*/\Delta = (1 + S)/(1 - S) > 1$, since $S > 0$.

If molecule XY is coordinated to atom M of the activator with formation of a linear fragment M-X-Y of local symmetry $C_{\infty v}$, then φ and φ^* can interact with corresponding σ and/or π orbitals of atom M. Three-center interactions M-XY can be described through matrix elements of two-center interactions M-X and M-Y:

$$\begin{aligned} \beta &= \langle \chi_M | \mathbf{H} | \varphi \rangle = [2(1 + S)]^{-1/2} [\langle \chi_M | \mathbf{H} | \chi_1 \rangle + \langle \chi_M | \mathbf{H} | \chi_2 \rangle], \\ \beta^* &= \langle \chi_M | \mathbf{H} | \varphi^* \rangle = [2(1 - S)]^{-1/2} [\langle \chi_M | \mathbf{H} | \chi_1 \rangle - \langle \chi_M | \mathbf{H} | \chi_2 \rangle]. \end{aligned}$$

Since interaction between the noncontacting atoms M and Y is considerably weaker than between the neighboring atoms M and X, then:

$$\begin{aligned} \langle \chi_M | \mathbf{H} | \chi_1 \rangle &\gg \langle \chi_M | \mathbf{H} | \chi_2 \rangle \\ (\text{since in the limit } \langle \chi_M | \mathbf{H} | \chi_2 \rangle &= 0) \end{aligned}$$

and, therefore,

$$\beta^2/\beta^2 \cong (1 + S)/(1 - S) \text{ or } \beta^{*2}/\beta^2 \cong \Delta^*/\Delta.$$

Further, the interaction M-XY is much weaker than the bond energy in XY ($SM-X \ll SX-Y$) and can be considered as a bonding perturbation in molecule XY. Therefore, the contributions Q and Q^* to the energy of the interaction M-XY from the occupied bonding φ and the vacant antibonding φ^* MOs of XY

can be described in terms of the first-order perturbation theory:

$$Q = \beta^2/(\varepsilon_M - \varepsilon), \text{ reflexes the electron transfer } \mu \leftarrow X_2 \text{ (0:2),}$$

$$Q^* = \beta^{*2}/(\varepsilon^* - \varepsilon_M), \text{ reflexes the electron transfer } \mu \rightarrow X_2, \text{ (2:0).}$$

where ε_M is the energy of valent AOs of M.

From here

$$Q^*/Q = \beta^{*2}(\varepsilon_M - \varepsilon)/\beta^2(\varepsilon^* - \varepsilon_M).$$

Accounting for

$$\beta^{*2}/\beta^2 \cong \Delta^*/\Delta = (\alpha - \varepsilon^*)/(\varepsilon - \alpha),$$

we obtain

$$Q^*/Q \cong (\alpha - \varepsilon^*)/(\varepsilon_M - \varepsilon)/(\varepsilon - \alpha)(\varepsilon^* - \varepsilon_M)$$

or

$$Q^*/Q \cong (\varepsilon^* - \alpha)/(\varepsilon - \varepsilon_M)/(\varepsilon - \alpha)(\varepsilon^* - \varepsilon_M).$$

If $\varepsilon_M > \alpha$, then $(\varepsilon - \varepsilon_M)/(\varepsilon - \alpha) > 1$, $(\varepsilon^* - \alpha)/(\varepsilon^* - \varepsilon_M) > 1$, and, totally, $Q^*/Q > 1$ at $\varepsilon_M > \alpha$; by contrast, $Q^*/Q < 1$ at $\varepsilon_M < \alpha$.

Typically, the energies ε_M of valent orbitals of atoms M are higher than the energies α of valent orbitals of atoms X and Y, constituting molecule XY, i.e. $\varepsilon_M > \alpha$. For this reason, one can conclude that the antibonding φ^* states of XY contribute most to the stabilization energy of M-XY and, therefore, to the destabilization energy of XY. This situation most frequently arises when XY coordinates to atoms M incorporated into cluster complexes of transition metals, since atoms M in clusters are in low oxidation states and contain, as rule, several electrons on their valent d orbitals, and, over all, are characterized by essentially heightened energies of HOMOs [3]. If XY coordinates to transition metal complexes ML_k with high oxidation states of M and, as a consequence, with reduced energies of valent orbitals of the latter (up to $\varepsilon_M < \alpha$), as well as a low d -electron population and with many vacant d AOs, the stabilization energy of M-XY is mostly contributed by the bonding φ MOs of XY.

Thus, vacant antibonding states of σ^* or π^* type often contribute most to the activation both of traditional acceptors S with low-lying vacant π^* MOs, and traditional donors S with high-lying vacant σ^* MOs. At least in the case of cluster complexes of transition

metals, the activation of multiple bonds in small molecules XY with closed shells, on their coordination with cluster atoms M, is mainly produced by filling earlier vacant antibonding σ^* and/or π^* MOs. Naturally, a certain contribution comes from decreasing electron population of highest occupied bonding MOs (synergistic effect).

Thus, the description of electron-donor and electron-acceptor interactions between a center and a coordinated molecule, within the frames of the valent approximation of the MO theory and the perturbation theory allows one to compare the contributions to the energy of the K–S interaction from bonding and antibonding frontier MOs of S and to gain insight into the nature of the attendant redistribution of valent electron density. The dominating process is two-electron transfer from the center to the coordinated molecule. Such electron pair is often delocalized over two or several atoms M of the cluster complex and is essentially destabilized as compared with the unshared electron pair of a free atom M. Many-electron (for example, four-electron) transfers are also possible.

A decisive factor of the activation of S is electronic donor–acceptor interactions between activator K and coordinated molecule S. The activation of a small molecule XY (destabilization of the multiple bond X–Y) is mainly caused by electron transfer from the activator to vacant antibonding MOs of the molecule coordinated to atoms M, i.e. by filling vacant antibonding MOs with valent electrons. From this a simple and useful conclusion follows: The electronic (most frequently, π -type) factors most favorable for activation of small molecules are the preferential acceptor ability of substrate molecule S and the donor ability of coordinating center K.

The proposed model is simple and has led to a simple and even expected conclusion. However, this conclusion is now theoretically correct and can be used for searching for optimal activators and catalysts (among transition metal compounds) for a certain chemical reaction involving small molecules.

To make the developed concepts more complete and more rigorous, it is reasonable to add the following. Generally, coordination-induced redistribution of valent electron density ($K \rightarrow S$ or $K \leftarrow S$) is certainly determined by several factors. One of the main factors is the formal valency of the coordinating atom. As a rule, the redistribution of type $K \rightarrow S$ prevails in cluster complexes of formally zero-valent transition metals with strong-field ligands [for example, $\text{Co}_2(\text{CO})_8$]. The redistribution of type $K \leftarrow S$ can dominate at increased oxidation degrees and, therefore, enhanced acceptor properties of atoms M [as, for

example, in $\text{Fe}_2(\text{CO})_6\text{Br}_2$]. In addition, to really and purposively increase the reactivity of a molecule to be coordinated may require different electron charge transfers. For example, the transfer $K \rightarrow S$ is important for activation of coordinated CO molecule in its reactions with electrophiles. At the same time, the transfer $K \leftarrow S$, enhancing the electrophilicity of alkenes or alkynes, is more important for activation of coordinated alkenes or alkynes in their reactions with nucleophiles.

Below are summarized the results of theoretical and experimental investigations of activation of CO, N_2 , H_2O , and N_3^- molecules mainly by molybdenum clusters.

ACTIVATION OF SMALL MOLECULES ON COORDINATION TO ATOMS M IN CLUSTERS. THEORY OF DELOCALIZED MO

Potential energy surface for interaction of an N_2 molecule with a Mo_2 binuclear cluster was calculated for various linear and nonlinear geometric configurations and by varying all (N–N, Mo–Mo, Mo–N) internuclear distances over a wide range [4]. The calculation results show that effective electron interactions arise when the diatomic particles N_2 and Mo_2 approach each other (the first valley on the potential energy surface) at a distance of 2.0–1.8 Å only at a perpendicular mutual orientation (C_{2v} symmetry of tetraatomic groups, Fig. 1). These effective electron interactions show up in displacement of the electron density from the Mo–Mo bond (highly multiple, many-electron, with σ , π , and δ components in the initial cluster Mo_2) to antibonding MOs of the molecule N_2 . A saddle arises on the potential energy surface; N_2 and Mo_2 stop to approach each other, and the N–N bond begins to strongly lengthen (second valley on the potential energy surface) to attain values considerably exceeding those characteristic of an even weak single interaction N–N. This implies an almost complete N–N bond cleavage. The calculated potential energy surface allowed estimation of activation energy (E_a) for the cleavage of the molecule N_2 on its interaction with the binuclear molybdenum cluster Mo_2 . Figure 2 represents the cross section of the potential energy surface along the reaction coordinate. The activation energy is estimated at 40 kJ, which is too low compared with the dissociation energy of the triple bond (953 kJ) in a free nonexcited ($^1\Sigma_g^+$) N_2 molecule.

Quantum-chemical calculations of the electronic structure of the model complex $[\text{Mo}_2\text{Cl}_8(\text{N}_2)]^{3-}$ in the spiro form (with symmetry C_{2v} completely analogous to represented in Fig. 1) with varied N–N and Mo–N internuclear distances were performed in [4]. Analysis

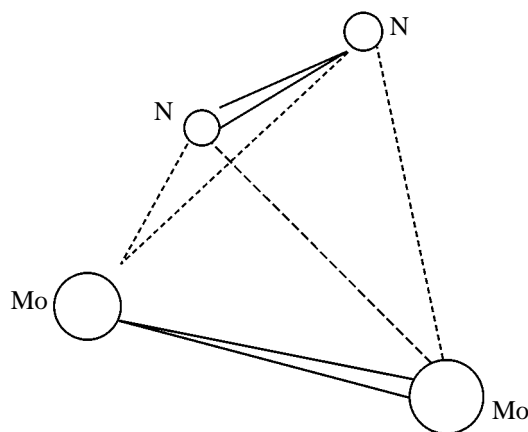


Fig. 1. Geometry of the tetraatomic group $[\text{Mo}_2\cdots\text{N}_2]$.

of the resulting energies and electron populations of MOs of N–N, Mo–N, and Mo–Mo showed that the coordination of the nitrogen molecule to the stereochemically open cluster $[\text{Mo}_2\text{Cl}_8]^{3-}$ gives rise to a considerable destabilization of N_2 just in this nonlinear geometry because of the effective pumping of electron density from the initially multiple (triple, six-electron) Mo–Mo bond of the cluster to antibonding π^* MOs of N_2 with simultaneously decreasing electron population and multiplicity of the Mo–Mo bond and arising Mo–N σ interaction. By contrast, N_2 is much destabilized in the binuclear complex $[(\text{P}_4\text{Cl})\text{Re}(\text{N}_2)\text{Mo}(\text{OCl}_4)]$ with a linear $\text{Re}-\text{N}-\text{N}-\text{Mo}$ group. In the electronic structure of this complex, quite a strong multiple (practically triple as in a free N_2 molecule) N–N bond is preserved, with dominating π_1 and π_2 contributions and with an only slightly weakened σ interaction. The preservation of the fragment N_2 in this complex is explained by a weak interaction of valent electrons of atoms M (Mo, Re) with vacant antibonding orbitals of N_2 . Thus, comparison of the electronic structures of the two calculated binuclear complexes of heavy transition metals with molecular nitrogen reveals principal differences in the character of electronic interactions of the N_2 molecule with two atoms M in these complexes in response to two interrelated factors, namely, the way of coordination of the N_2 molecule in the complex with respect to the two M atoms and the presence or absence of an M–M bond in the complex (i.e. in response to the cluster effect). The N_2 molecule is strongly destabilized only if it coordinates to a cluster with a multiple, many-electron M–M bond in a nonlinear geometry, i.e. in the spiro form. By contrast, N_2 remains almost inactivated when it linearly coordinates to a binuclear complex with no M–M bond.

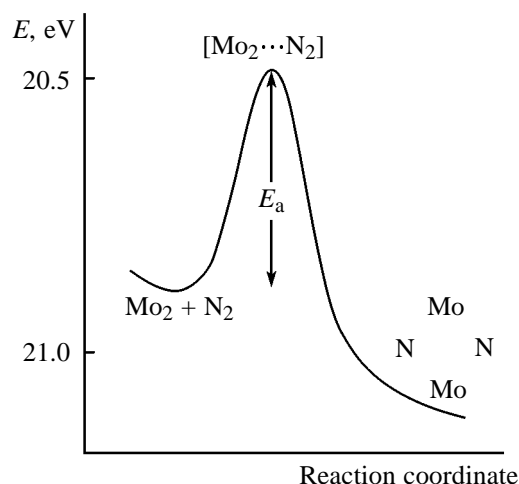
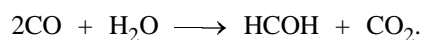
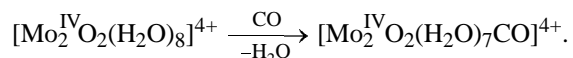


Fig. 2. Energy profile for the reaction of N_2 with Mo_2 .

When activated with binuclear di- μ -oxomolybdenum clusters, carbon monoxide transforms to formaldehyde in aqueous solutions [5]:

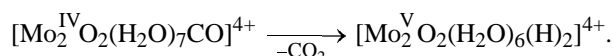


To ascertain the reaction mechanism, the potential energy surface of the reaction of CO and H_2O molecules in the coordination sphere of catalytically active $[\text{Mo}_2^{\text{IV}}\text{O}_2(\text{H}_2\text{O})_8]^{4+}$ was calculated and analyzed [5]. As based on the results of quantum-chemical calculations, the mechanism of this reaction can be represented as follows. The CO molecule coordinates to the cluster via inner-sphere replacement of one H_2O molecule (Fig. 3, point 2):

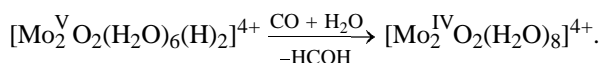


The electron density of the double ($\sigma + \pi$) cluster bond Mo–Mo is effectively displaced to antibonding π^* MOs of the CO molecule, and the CO group is destabilized. Then the CO group and the *cis*- H_2O molecule pass to bridging positions. The originally planar central Mo_2O_2 fragment is distorted. The O–H bonds in the H_2O molecule are stretched. Hydrogen atoms occupy coordination sites originally occupied by the H_2O and CO molecules. All these steps lead to the main energy barrier and to appearance of a $[\text{Mo}_2^{\text{IV}}\text{O}_2(\text{H}_2\text{O})_7\text{CO}]^{4+}$ transition complex (Fig. 3, point 3). On formation of the bridging bond M–CO–M (including σ -donor and π -acceptor interactions) in this complex, the electron density of the M–M bond is displaced to the CO group, resulting in further effective destabilization of the two-center M–M and C–O bonds. Further on, two Mo–H bonds

begin to form in the transition complex. Simultaneously, both O–H bonds in the bridging H₂O molecule are weakened, a bond arises between one O atom of this H₂O molecule and the carbonyl C atom to form still a nonlinear CO₂ group, the M–M bond is cleaved completely, and both M–C bonds begin to disappear. Finally, translation and removal of the CO₂ molecule occur, restoration of the M–M bond, and formation of a [Mo₂^VO₂(H₂O)₆(H₂)₂]⁴⁺ binuclear hydride cluster:



This is the first stage $\text{CO} + \text{H}_2\text{O} + \text{K} = \text{CO}_2 + \text{K}(\text{H})_2$. After this, the hydride cluster interacts, by its HOMO, with a second CO molecule. This HOMO, with an energy of about –10 eV, corresponds to the interaction M–M, its electron density is concentrated just between hydride H atoms and is accessible for attack of the second CO molecule with the resulting two-electron reduction of carbon monoxide to formaldehyde and relaxation of the cluster catalyst:



This is the second stage $\text{CO} + \text{K}(\text{H})_2 = \text{HCOH} + \text{K}$, and, as a whole, $2\text{CO} + \text{H}_2\text{O} = \text{HCOH} + \text{CO}_2$. The second stage can be different and involve hydrolysis of the intermediate hydride cluster with removal of a hydrogen molecule, subsequent coordination of two H₂O molecules, and recovery of the initial catalytically active cluster: $\text{K}(\text{H})_2 = \text{H}_2 + \text{K}$, and, as a whole, $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. Therefore, the reduction of CO to formaldehyde is always accompanied by conversion of water gas, including the same first stage.

ACTIVATION OF SMALL MOLECULES ON COORDINATION TO ATOMS M IN CLUSTERS. ONE-PARAMETER VARIANT OF THE VIBRONIC THEORY OF ACTIVATION

A cardinal moment of the vibronic theory of coordination-induced activation is that vibronic effects (nuclear displacements and, first of all, increase in internuclear distances, decrease in force constants and bond energies, decrease in activation energy, i.e. reactivity enhancement for certain mechanisms of reactions of coordinated molecule) are a consequence of electronic rearrangements in coordinated molecule. In their turn, the electronic rearrangements are caused by the charge transfers produced by coordination of the molecule to a coordinating center and, therefore, by variations (increases or decreases) in the electron population of MOs of the molecule as compared with corresponding characteristics of the molecule in its free state [6–8].

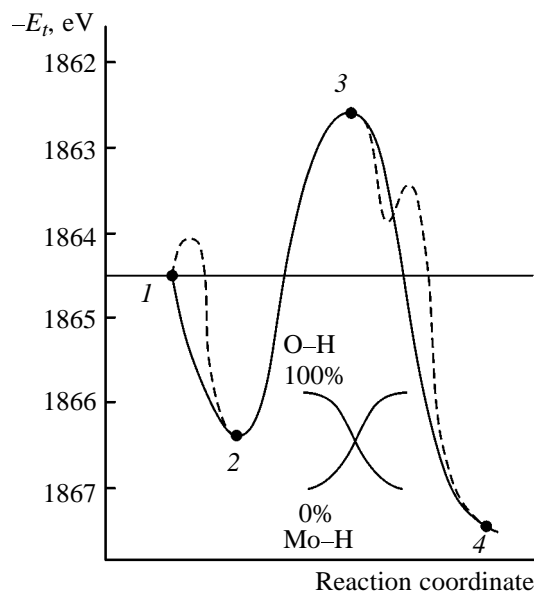


Fig. 3. Energy profile for the reaction $\text{CO} + \text{H}_2\text{O}$ along the reaction coordinate and variation in the population of O–H and Mo–H bonds near the activation barrier. The dash line shows possible local barriers for intra-spherical replacement of H₂O by CO in the cluster catalyst and for removal of CO₂. (1) [Mo₂^{IV}O₂(H₂O)₈]⁴⁺ + CO; (2) [Mo₂^{IV}O₂(H₂O)₇CO]⁴⁺ + H₂O; (3) Transition complex [Mo₂^{IV}O₂(H₂O)₇CO]⁴⁺ + H₂O; and (4) [Mo₂^VO₂(H₂O)₆(H)₂]⁴⁺ + CO₂ + H₂O.

The coordination-induced electron density redistribution in a molecule (i.e. changed electron distribution, new values of orbital populations, and, as a whole, electronic rearrangement) leads to appearance of a non-zero deforming force in the symmetrized direction Q_α : $F_\alpha = \sum_i \Delta g_i f_\alpha^i \neq 0$. This force changes the nuclear configuration of the coordinating molecule as compared with the equilibrium nuclear configuration of the free molecule, increases internuclear distances, and decreases force constants. All these effects decrease the activation energies of reactions of the coordinated molecule, reactions involving nuclear displacements in certain directions (regulated by the symmetry of the i th MO), and, as a whole, enhance the reactivity of the coordinated molecule.

In the vibronic theory of activation, changes in the activation energy are determined from theoretically computed orbital vibronic constants of a coordinated diatomic molecule and from its two experimental parameters, the equilibrium internuclear distance R and the force constant K (or, which is the same, the stretching vibration frequency ν). Herewith, the quantities R and K (or ν) are assumed to be independent. In reality, these two quantities are not independent.

Rigorously accounting for the interrelation between the force constant or the stretching vibration frequency of a diatomic molecule and its internuclear distance $K = f(R)$ or $\nu = f(R)$, a one-parameter variant of the vibronic activation theory was developed [9, 10]. In this variant, a decisive characteristic of coordination-induced activation of a molecule, the activation energy E_a of a reaction involving this coordinated molecule, can be calculated using only one parameter: K , ν , or R .

The calculation is based on dependences [7] including the activation energy of the same process involving the free molecule, the force constants of the free and coordinated molecule, the equilibrium internuclear distances of the free and coordinated molecule, and the ratio of the anharmonicity constants. Using the one-parameter variant of the vibronic theory of activation, we calculated and described the activation of several homonuclear and heteronuclear diatomic molecules on their coordination to atoms M in many cluster complexes of transition metals. The most detail study concerned the vibronic activation of the CO molecule [9, 10] with a triple $(\sigma + 2\pi)$ six-electron $\text{C}\equiv\text{O}$ bond having a very high energy (1070 kJ) and a very short internuclear distance (1.12 Å). For this molecule, the electron population P of its frontier MOs (bonding HOMO 5σ and antibonding LUMO $2\pi^*$) and the orbital charge transfers Δq on them are related by simple evident relationships reflecting the electron populations of the 5σ ($2\bar{e}$) and $2\pi^*$ ($0\bar{e}$) MOs in a free nonexcited CO molecule:

$$-2 < \Delta q_{5\sigma} < 0, 0 < \Delta q_{2\pi} < 4, P_{5\sigma} = 2 + \Delta q_{5\sigma}, \\ P_{2\pi^*} = \Delta q_{2\pi}.$$

On interaction of the molecule CO with atoms M (on overlap of their valent orbitals), a certain fraction of electron charge is transferred the bonding $5\sigma(\text{CO})$ MO to vacant σ orbitals of atoms M and, simultaneously, from occupied π orbitals of atoms M to the vacant antibonding $2\pi^*(\text{CO})$ MO. The lowering of the electron population of the bonding MO and the simultaneous heightening of the electron population of the antibonding MO of the CO molecule on its coordination to atoms M steeply decrease the multiplicity and energy of the C–O bond and increases the C–O internuclear distance as compared with a free CO molecule.

Analysis of the resulting data allowed the following conclusions [9, 10]. The activation of the CO molecule is mostly influenced by the way of its coordination to the Mn group: terminal or μ_2 -, μ_3 -, or μ_4 -bridging (in ascending order) or more complex variants, when the diatomic molecule CO is coordi-

nated to the Mn group in such a way that not only its atoms (C and O), but also the charge density of the previously triple $(\sigma + 2\pi)$ $\text{C}\equiv\text{O}$ bond turn to be bound with several cluster atoms. For example, one of the most effective activations is observed when CO coordinates flatways to a triangular Nb_3 group incorporated in the trinuclear cluster $\text{Nb}_3(\pi\text{-C}_5\text{H}_5)_3(\text{CO})_7$. In this case, the CO molecule is coordinated so that the C atom is located over the center of the triangular Nb_3 group, and the C–O bond is located over the middle of one of the Nb–Nb edges. Experimental data show that here we deal with the strongest CO activation, since the CO stretching vibration frequency decreases (compared with the standard value 2170 cm^{-1}) to an abnormally low value of 1330 cm^{-1} and the force constant of the C–O bond decreases almost 3-fold, from 19 to 7 mdyne/Å. The same conclusions follow from the results of calculations by methods of vibronic theory: Practically both electrons are transferred from the 5σ orbital of the CO molecule to Nb_3 (the σ bond disappears), 1.8 electrons are transferred from the Nb_3 group to the antibonding $2\pi^*$ orbital of the CO molecule (one of the two π bonds almost disappears). With this, the multiplicity of the C–O bond decreases almost 3-fold (from triple to almost single), the bond energy becomes 5–6 times lower, the C–O internuclear distance steeply increases. All in all, it is clear that the destabilization of the CO molecule is so strong that one can say about its dissociation into to weakly bound atoms (C and O). As shown by the above theoretical calculations, we deal here with a rare case when an abnormally high activation of the coordinated molecule is caused by change in the electron population of its not only frontier orbitals (one HOMO and one LUMO), but also of the second occupied bonding ($1\pi^4$) orbital. From the latter MO, a small fraction of electron charge is transferred to the Nb_3 group, which additionally decreases the multiplicity and energy of the C–O bond and enhances destabilization of the coordinated CO molecule. Herewith, however, the C and O atoms simultaneously form very strong bonds with cluster Nb atoms. Therefore, this is just that case when a very strong destabilization of coordinated molecule does not enhance its reactivity: The CO group of the $\text{Nb}_3(\pi\text{-C}_5\text{H}_5)_3(\text{CO})_7$ cluster fails to react with H_2 and some other reagents.

CATALYTIC HOMOGENEOUS REACTIONS OF SMALL MOLECULES, ACTIVATED BY CLUSTER COMPLEXES

The activation of a molecule coordinated to a cluster directly enhances the reactivity of the former and, in some cases, favor a reaction which turns to be completely catalytic, provided the cluster activator

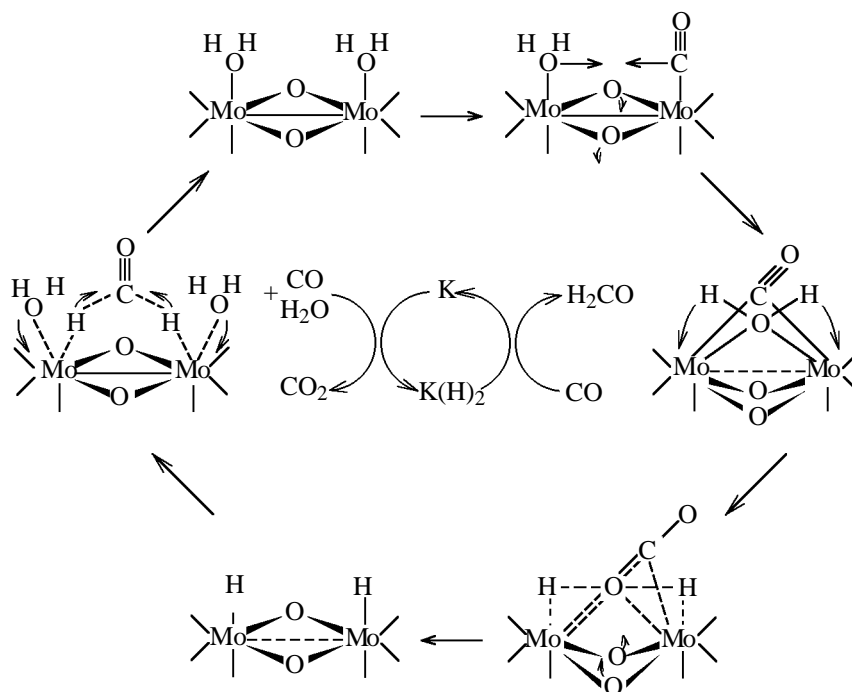
relaxes. If molecule S coordinates to one or several atoms M of a cluster complex, there occurs weakening or even rupture of strictly definite bonds in the coordinated molecule. In principle, this secures the possibility of subsequent chemical transformation of the molecule, of its interaction with a reagent R: $S + R \rightarrow P$ (P is reaction product). The decisive condition here is that the complex of molecule S with the cluster is strong enough in the sense that the strength of bonding between the molecule (or its fragments) and atoms M is high enough to form such a complex (otherwise, there will be no coordination): $M + S \rightarrow MS$, but not too high to produce critically large values of the enthalpy and energy of activation on the stage of interaction of the coordinated molecule with the given reagent: $MS + R \rightarrow P + M$.

The activation of a molecule on its coordination to a cluster complex can be traced by the increasing internuclear distances and by the decreasing stretching vibration frequency and can be quantitatively described in terms of various quantum-chemical approaches: the MO theory, the potential energy surface theory, or the vibronic theory. The occurrence of catalytic reactions is a directly observable consequence of the activation under discussion. The catalytic ability of cluster complexes of transition metals is especially pronounced in the case of redox reactions and, first of

all, with respect to electron-transfer redox cleavage of small molecules with especially strong multiple bonds: N_2 , CO, NO, N_3^- , NO^+ , RNC, CN^- , RN_2^- , $RC \equiv CR$, etc. Activation of these multiple bonds (for example, on their two- or many-electron reduction) depends on the individuality of cluster complexes (number, nature and formal valency of M atoms in the Mn group, and ligand type), on the geometric and electronic structure of cluster complexes, on the type of coordination of activated molecule with the Mn group, and on other factors. Heterogeneous and homogeneous catalytic redox reactions of small molecules involving cluster complexes of transition metals are known. There are only few homogeneous catalytic reactions, activated by cluster complexes, which have been investigated in detail (including mechanisms).

Using chromatographic methods, the reduction of carbon monoxide to formaldehyde in aqueous solutions under ordinary (mild) conditions $2CO + H_2O \rightarrow HCOH + CO_2$, activated by binuclear di- μ -oxo clusters of tetravalent molybdenum, was discovered and studied [5]. Simultaneously, the water gas conversion $CO + H_2O \rightarrow CO_2 + H_2$ proceeds in this system. The transformation of CO into formaldehyde under ordinary conditions has been realized for the first time. This is the discovery of a new and useful type of redox CO cleavage, not related directly to known Fischer-Tropsch catalytic CO conversions.

Scheme 1.



Thus, the reactions $2\text{CO}(\text{gas}) + \text{H}_2\text{O}(\text{l}) = \text{CO}_2(\text{gas}) + \text{HCOH}(\text{aq})$ ($\Delta G^0 = -12 \text{ kJ/mol}$) and $\text{CO}(\text{gas}) + \text{H}_2\text{O}(\text{l}) = \text{CO}_2(\text{gas}) + \text{H}_2(\text{gas})$ ($\Delta G^0 = -20 \text{ kJ/mol}$), thermodynamically allowed but not realizable under ordinary conditions, proceed fast in the presence of the binuclear cluster $[\text{Mo}_2^{\text{IV}}\text{O}_2(\text{H}_2\text{O})_8]^{4+}$ and are really catalytic (the theoretically calculated mechanism of the process is described above). On the basis of the temperature dependence of the rate of the disproportionation of CO, catalyzed by binuclear clusters of tetravalent molybdenum, the activation energy was estimated at $35 \pm 10 \text{ kJ/mol}$ [5]. Although being approximate, experimentally estimated E_a values are clear to be negligible in comparison with the bond energy in the CO molecule (1070 kJ/mol). This gives evidence for a practically crushing effect of the $[\text{Mo}_2^{\text{IV}}\text{O}_2(\text{H}_2\text{O})_8]^{4+}$ cluster on the CO molecule, leading to a dramatic (as a result of activation) decrease in the activation barrier for disproportionation of carbon monoxide with its reduction to formaldehyde.

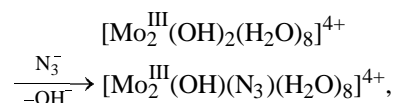
Formal kinetics methods and UV, IR, and X-ray photoelectron spectroscopy were used to study the reduction of the azide anion to ammonia with borohydride in aqueous solutions, catalyzed by binuclear

di- μ -oxo(hydroxo) clusters of low-valent molybdenum [11–14].

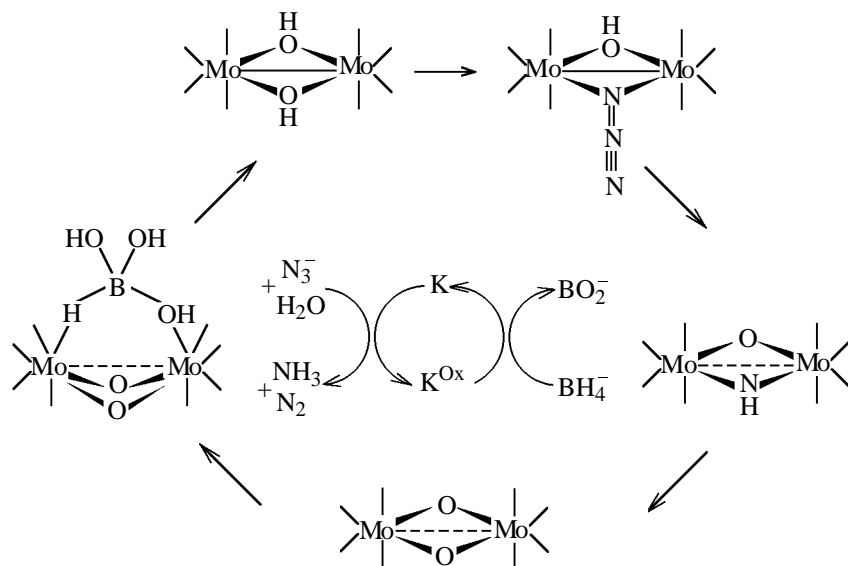


The azide anion N_3^- has a linear geometry and a hypervalent electronic structure with two two-center covalent σ bonds and two three-center hypervalent π bonds, so that the multiplicity of each (of the two) two-center interactions is somewhat higher than 2 [15, 16]. The total energy of all the bonds is high, no less than 600 kJ/mol; the azide anion is stable and does not take part in redox reactions in aqueous solutions in the absence of catalysts.

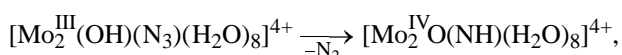
The reduction of the azide anion by borohydride proceeds easily and fast under activation with binuclear di- μ -hydroxo clusters of trivalent molybdenum [2, 12], which contain a triple ($\sigma + 2\pi$) M–M bond and are strong electron donors. The main consecutive stages of the redox process are (Scheme 2) coordination of the N_3^- anion to two Mo atoms in the μ_2 position in the course of replacement of one hydroxo group



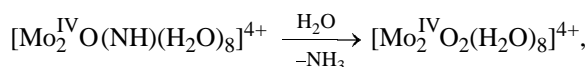
Scheme 2.



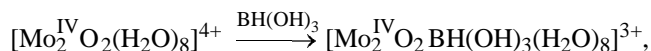
intermolecular reduction of N_3^- to $=\text{NH}$ with N_2 liberation, and simultaneous oxidation of both Mo atoms from the trivalent to tetravalent state



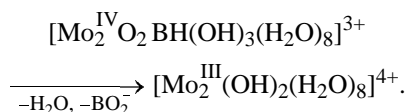
hydrolysis of the resulting Mo–NH–Mo group with NH_3 liberation



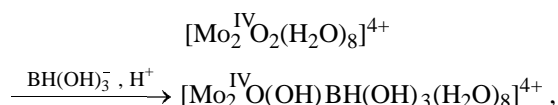
coordination of the borohydride anion to the Mo_2O_2 group of the cluster



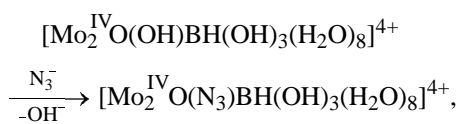
and reduction of both Mo atoms to the initial trivalent state via oxidation of the hydride hydrogen and return to the initial state of the cluster catalyst



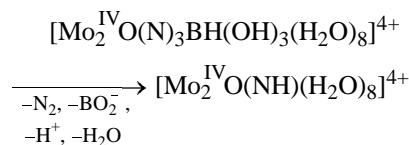
The same reaction also proceeds under activation by binuclear di- μ -oxo clusters of tetravalent molybdenum [2, 13, 14] containing a double ($\sigma + \pi$) M–M bond and possessing a somewhat lower electron-donor ability. In this case, the main stages of the redox reaction are (Scheme 3) preliminary coordination of the borohydride anion to the Mo_2O_2 group of the cluster and protonation of one of the bridging oxygen atoms in this group



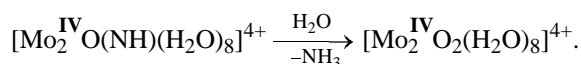
coordination of the N_3^- anion on this group in the μ_2 position in the course of substitution of the hydroxo group formed by protonation



intermolecular two-electron transitions in the resulting ternary complex with oxidation of the hydride hydrogen and reduction of N_3^- to $=\text{NH}$ with N_2 liberation (limiting stage)



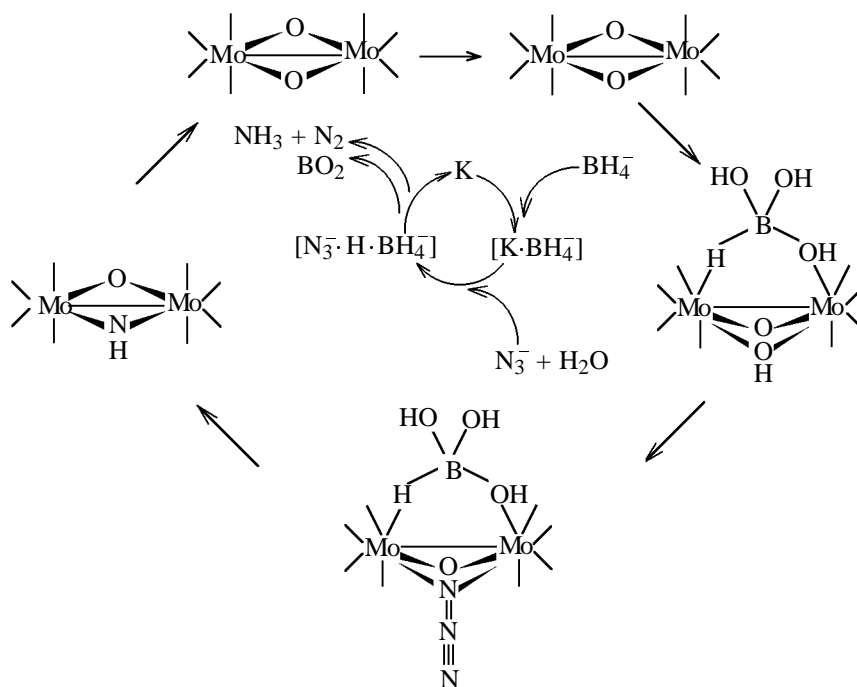
and, finally, hydrolysis of the resulting Mo–NH–Mo group with NH_3 liberation and return of the cluster catalyst to the initial state



PHOTOCATALYTIC DECOMPOSITION OF WATER ON CLUSTERS

Electronically excited clusters are much more potent activators of coordinating molecules and thus much more potent catalysts of corresponding reactions. Such clusters possess stronger electron-donor (due to the appearance of electrons on vacant MOs with heightened energies) and electron-acceptor properties

Scheme 3.



(due to the appearance of vacancies on occupied MOs with lowered energies). All this promotes corresponding electron transfers in complex KS, which are necessary for destabilization of molecule S coordinated to the M_n group of the cluster.

We have studied the photocatalytic decomposition of water into gaseous hydrogen and oxygen (whose formation was registered by mass spectrometry on omegatron), activated by cluster complexes adsorbed on Silochrom [17]. The adsorbed state favored stabilization of the clusters in the photochemical redox process and spatial separation of simultaneous elementary acts of hydrogen and oxygen formation.



The spectral region of photocatalytic activity of clusters ranging from 640 to 1000 nm is the most interesting. The photocatalytic decomposition of water in a wide spectral range at $\lambda > 640$ nm was observed in the case of cluster complexes of heavy transition metals (molybdenum and rhenium) with the weak-field ligands $[\text{Mo}_2\text{Cl}_8]^{4-}$, Re_3Cl_9 , and, partly, $[\text{Mo}_2\text{O}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_4]$. Their characteristic features are as follows. Firstly, the clusters possess a large number of valent d electrons in MOs localized on the M–M bonds: $8(\sigma + 2\pi + \delta)$, $12(3\sigma + 3\pi)$, and $4(\sigma + \pi)$, respectively, which secures the possibility of effective interaction of these electrons with antibonding orbitals of the H_2O molecule on its coordination to a cluster. Secondly, the clusters are characterized by various electron transitions in a wide spectral range. Thirdly, the clusters possess a sterically open form which allow the H_2O molecule to coordinate to that cluster region where the electron density of the M–M bonds is concentrated. Of particular importance is that these clusters contain π even δ electrons whose charge density is spread beyond the limits of the M_n (M_2 , M_3) group. The regions of distribution of the π - and δ -electron density in these clusters are quite accessible for coordinating the H_2O molecule or its fragments.

Irradiation of samples (clusters $[\text{Mo}_2\text{Cl}_8]^{4-}$ and Re_3Cl_9 , adsorbed on Silochrom in water vapor) at $\lambda > 640$ nm led to fast decomposition of water into hydrogen and oxygen (up to 10^{15} molecule/s for H_2). The dependence of the rate of the photodecomposition of H_2O on the light intensity is essentially nonlinear: $d[N]/dt \sim I^n$ at $n = 4$, which points to a multiquantum character of the process.

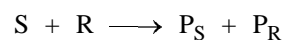
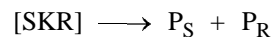
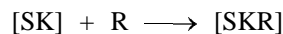
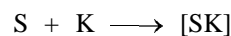
All in all, the results obtained give evidence showing that $4d$ - and $5d$ -element clusters with weak-field ligands, adsorbed on SiO_2 , are effective catalysts of photodecomposition of water. The photocatalytic process is essentially dependent on the electronic and

geometric structures of the clusters (many valent d electrons in MOs localized on M–M bonds and sterically open form). Herewith, clusters able to secure many-electron and multiquantum processes photocatalytically decompose coordinated water without auxiliary electron donors and acceptors and without additional catalysts of formation of hydrogen and oxygen. The sorption of a cluster on a support inevitably lifts degeneracy of many MOs, makes certain MOs closer in energy, and increases the number of allowed, first of all, low-energy transitions. Probably, this is one of the main reasons why support favors enhanced photocatalytic activity of clusters.

MODIFICATIONS OF HOMOGENEOUS CLUSTER CATALYSIS OF REDOX REACTIONS OF SMALL MOLECULES

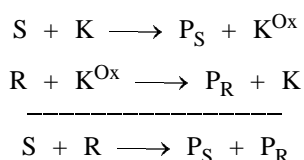
The electronic effects of activation of small molecules by cluster complexes of transition metals and the resulting favorable combinations K–S (K is a strong or a weak donor, S is a strong or a weak acceptor) predetermine the existence of several modifications of homogeneous cluster redox catalysis.

First modification. For activating small molecules with strong π -acceptor properties and with low energies of LUMOs, such as CO and NO^+ , the weak donor ability of many clusters will suffice. Activation of such molecules only slightly depends on donor properties of the clusters. The typical features of this modification of cluster redox catalysis are the following: (1) activation occurs as a result of coordination of the substrate molecule to atoms M of the cluster catalyst; (2) transition complex is formed by rearrangement in the inner coordination sphere of the cluster; (3) electron transitions occur in the transition complex, and the cluster activator acts as electron redistributor; (4) the degree of oxidation of atoms M in the cluster (the electron population of MOs localized on M–M bonds and the multiplicity of the M–M bonds in the transition complex are much decreased) changes in the course of the catalytic act; and (5) the monomolecular stage of rearrangement and decomposition of the transition complex is often limiting:



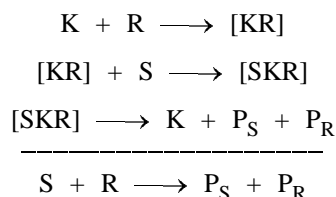
The activation of the CO molecule on its coordination to binuclear clusters of tetravalent molybdenum belongs to this category.

Second modification. For activating small molecules with weak π -acceptor properties and with higher, than in the first case, energies of LUMO, such as N_2 , N_3^- , and CN^- , clusters possessing very strong donor properties are needed, with an especially low formal valency of atoms M, with a large number of valent d electrons in M–M bonds, with highly multiple two-center M–M bonds, and with heightened energies of MOs localized on M–M bonds. The typical features of this modification of cluster redox catalysis are the following: (1) activation occurs as a result of oxidative addition of the substrate molecule to the cluster catalyst; (2) electron transitions occur in bimolecular limiting stages; (3) the catalytic role of the cluster is to carry electrons from the reducing reagent to the substrate; (4) the degree of oxidation of atoms M in the cluster increases in intermediate stages of the catalytic process, while the electron population of MOs localized on M–M bonds and the multiplicity of the latter decrease; and (5) the reducing reagent causes relaxation of the cluster catalyst to its initial state:



The activation of the anion N_3^- on its coordination to binuclear clusters of trivalent molybdenum belongs to this category.

Third modification. A molecule with a low electron-acceptor ability cannot be activated by a weakly donor cluster, but activation becomes possible when the donor ability of the cluster is enhanced by complex formation with a strong electron donor (reducing agent). The typical features of this modification of cluster redox catalysis are the following: (1) activation occurs as a result of heterolytic addition of the substrate molecule to a complex preliminary formed by the cluster and the reducing reagent (enhancement of donor properties of the cluster activator); (2) electron transitions are realized in the resulting triple complex and are purely intermolecular; (3) the catalytic role of the cluster catalyst is to redistribute electrons (the main unit is the M–M bond system in the cluster); (4) the limiting stage is monomolecular and corresponds to decomposition of the triple complex after its electronic rearrangement; and (5) the degree of oxidation of atoms M in the cluster does not change in the course of the process; neither the electron population of MOs localized on M–M bonds, nor the multiplicity of the latter change essentially:



The activation of the anion N_3^- on its coordination to binuclear clusters of tetravalent molybdenum belongs to this category. The principal difference between the third and second modifications is that the base catalytic reaction in the third modification involves simultaneous coordination both of the substrate and the reducing reagent on the cluster catalyst, whereas the catalytic process in the second modification involves sufficiently isolated stages.

The above examples represent the main peculiarities of the mechanism of the catalytic action of cluster complexes of transition metals in redox reactions of small molecules, where the cluster activating the reaction plays the role of electron redistributor or carrier in oxidative, homolytic, or heterolytic addition reactions.

The peculiarities of the energetic distribution of valent electrons in clusters, the energies of their vacant MO, and the spatial characteristics of the distribution of charge density of valent electrons in cluster complexes of transition metals predetermine the high ability of these complexes to activate molecules coordinated to them [18, 19]. The presently available evidence (both experimental and theoretical) almost always shows that it is cluster complexes that much stronger activate any coordinated molecule than corresponding (the same transition metal in the same oxidation state and with the same ligands) mononuclear complexes. This is the so-called cluster effect. The most important factors of the cluster effect are the following: (1) the presence of a large number of valent d electrons of atoms M in M–M interactions in the M_n group (bonding regions in the Mn group, suitable for coordinating molecule S, low formal valence of atoms M); (2) significant electron-donor and electron-acceptor abilities of frontier MOs (HOMO and LUMO) in cluster M_nL_m , contributed mostly by valent d orbitals of atoms M and corresponding to the M–M interaction in the cluster; (3) many-orbital, many-electron, multicenter (i.e. involving many valent orbitals, electrons, and atoms) character of bonds between the atoms M of cluster M_nL_m and molecule S coordinated to it and the synergistic effect of two-sided transfers of valent electron charges, inherent in these σ and π interactions; (4) variety of structural characteristics of clusters M_nL_m , which favors optimal coordination of molecule

S; (5) special role of d orbitals of atoms M as channels for electron transfer to a given (necessary for occupation) region of space on electronic interactions of the cluster with the coordinated molecule; (6) lifting of symmetry forbiddenness for any subsequent reaction involving the coordinated and activated molecule, creating the most favorable, in terms of the rules of conservation of orbital symmetry, conditions for such a reaction.

The activation of molecule S on its coordination to a cluster, occurs, as a rule, via electron density transfer from occupied (often bonding) MOs of the cluster (to be more exact, of its M_n group) to unoccupied antibonding orbitals of molecule S. In other words, molecule S is preferentially activated by such orbital charge transfers that correspond to pumping electron density from the M_n group to antibonding MOs of the coordinated molecule S. Further, the activation is only slightly affected by the individuality of the cluster-forming transition metal. The activation strengthens (weakens) when cluster M_nL_m includes ligands with less (more) pronounced, compared with the coordinated molecule S, π -acceptor properties. Coordinated molecules are best activated by open clusters characterized by the absence of one or several atoms M in the "ideal" M_n polyhedron or by its strong spatial distortion, as well as by the absence of one or several ligands in the coordination sphere of one or another cluster atom M or by a strong distortion of the coordination sphere. Stereochemically open clusters feature a significant anisotropy (measure of nonspherical distortion) of distribution of valent electron density in the space of one or another atom M:

$$L_A = \sum_{\lambda \in A} \sum_{\lambda' \in A} p_{\lambda\lambda'}^2 - \sum_l \left(\frac{\lambda=(l+1)^2}{\sum_{\lambda=l^2+1} p_{\lambda\lambda}} \right) [1/(2l+1)],$$

where l is the orbital quantum number of the valent orbital of atom A, $p_{\lambda\lambda} = 1/2 \sum_{\sigma} p_{\lambda\sigma}^2$ are the elements of the density matrix $p_{\lambda\sigma} = 2 \sum_i c_{i\lambda} c_{i\sigma}$ in accordance with the Salem–Wyberg equation, and $\sum_{\lambda \in A} p_{\lambda\lambda}$ is the sum of all orbital densities over atom A.

The character and degree of activation of a molecule coordinated to a cluster complex can be varied (rather finely) in very wide limits by changing the nature of the transition metal, the number and valency of its atoms in the cluster, and also the type of ligands bound with them. Eventually that implies the principal possibility of predicting the direction of subsequent chemical transformation of the coordinated molecule and the rate of its reaction with a given reagent.

An important property of cluster complexes, based on the presence of several coordinating M centers in

the M_n group, is their ability to simultaneous coordination and activation both of coordinated (S) and reagent (R) molecules with subsequent reaction between these molecules in the "coordination sphere" of the cluster complex.

Cluster catalyst is a structurally nonrigid system which undergoes an essential electronic rearrangement in the course of the catalytic act. First of all, this is change in characteristics of M–M bonds until to their disappearance; therewith, the complex preserves its polynuclear structure due to bridging or polydentate ligands. The enhanced catalytic activity of cluster complexes, as compared with corresponding mononuclear complexes, in redox processes with two- or more-electron transfers is underlied by the ability of cluster complexes to effect (because of the presence of several atoms M) multicenter interactions with a coordinated molecule, thus facilitating many-electron processes.

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